AD NUMBER

AD866975

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies only; Administrative/Operational use; Jan 1970. Other requests shall be referred to U.S. Army Missile Command, Redstone Arsenal, Alabama 35809.

AUTHORITY

DoDD 5230.24, 18 Mar 1987.

AD

REPORT NO. RK-TR-70-6

CROSSLINK DENSITY DETERMINATIONS FOR POLYMERIC MATERIALS

by

Donald L. Martin, Jr.

January 1970

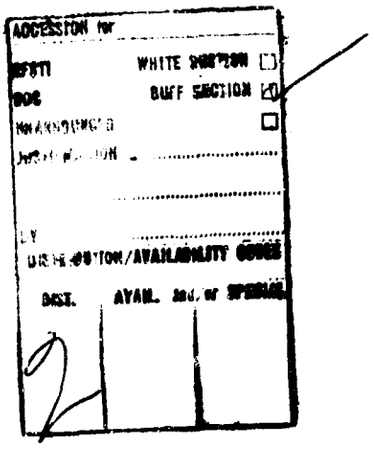
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of this Command, ATTN: AMSMI-RK.

U.S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama

3c

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.



DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed. Do not return it to the originator.

28 January 1970 Report No. RK-TR-70-6

CROSSLINK DENSITY DETERMINATIONS FOR POLYMERIC MATERIALS

by

Donald L. Martin, Jr.

DA Project No. 1M262302A211
AMC Management Structure Code No. 522C.11.585

Army Propulsion Laboratory and Center
Research and Engineering Directorate
U. S. Army Missile Command
Redstone Arsenal, Alabama 35809

ABSTRACT

Chemical crosslinking of polymeric binders is possibly the most significant factor affecting the mechanical behavior of unfilled and highly filled elastomers. There are basically two physical methods used by various investigators for experimentally determining the degree of crosslinking in elastomeric materials. These are the swelling method using Flory's equation and the equilibrium stress-strain method. The procedure discussed in this report is recommended as a tentative standard procedure to be followed in the collection of equilibrium stress-strain data and in the use of these data in the determination of the effective crosslink density of polymeric binders and composite propellants.

CONTENTS

ILLUSTRATIONS

Section I. INTRODUCTION

The requirement for some degree of permanence of structure in rubbery materials is usually achieved by the introduction of occasional chemical crosslinks between polymer chains. This results in a three-dimensional network in which a very large number of polymer molecules are joined together in one molecule of essentially inifinite molecular weight. The crosslinking or curing process prevents chain-chain slippage when deforming stresses are applied to the sample. Most rubber-based composite propellants are highly filled with crystalline and metallic particles. Failure in these composite materials originates at the filler particle or binder molecular level. The stress-strain response and failure properties of these materials have been shown to be dependent on the binder characteristic parameters such as crosslink density, volume fraction of extractables [1], and molecular weight distribution of the prepolymer used in the formulation [2]. The addition of rigid filler particles further amplifies the complexities of the response mechanism, and the deformation characteristics reflect the combined influence of both the binder and filler. Therefore, a structural definition of the binder network would be especially useful to the propellant technologist if the network's definitive property can be translated into meaningful property characteristics in some quantitative fashion. A method most commonly used to relate the binder network structure to mechanical behavior involves stress-strain measurements on a solvent-swollen specimen after equilibrium swelling has been obtained [3]. Section II contains the theory underlying the use of equilibrium stress-strain behavior to determine the crosslink density. In Section III the work of various investigators that have used this basic method is discussed. Section IV contains the experimental procedure recommended for adoption as a standard to be used by contractor and government installations. In Section V the procedure recommended in the treatment and reporting of the data is discussed, and in Section VI the statistical variation of some crosslink density data determined from equilibrium stress-strain measurements is given.

Section II. THEORY

A method most commonly used to relate the crosslink density of the network structure to mechanical behavior involves stress-strain measurements at equilibrium conditions. This method of determining the crosslink density may be related to two different theories. A Gaussian statistical network theory of rubber elasticity as proposed by Flory and Rehner [4] resulted in the relation

$$\frac{F}{A_i} = \nu_e RT(\lambda - \lambda^{-2}) \quad , \tag{1}$$

where

F = force (g/cm^2)

A_i = the initial cross-sectional area of the unstrained specimen (cm^2)

R = universal gas constant (8.479×10^4 gm-cm/mole, °K)

T = test temperature (°K)

λ = extension ratio.

This same method has been related to a non-Gaussian statistical theory of elasticity as proposed by Mooney [5] and Rivlin [6] and expressed by the equation

$$2C_1 + 2C_2/\lambda = \frac{F}{A_i}/(\lambda - \lambda^{-2}) \quad , \tag{2}$$

where C_1 and C_2 are independent parameters. C_1 has been defined as the Gaussian term $\left(C_1 = 1/2\ \nu_e/RT\right)$, and C_2 is related to the internal energy of the rubber contributed by the non-Gaussian characteristics. Although the constant $2C_2$ in Equation (2) has not been given full physical significance, it may be interpreted as a combination of factors which cause deviation of the real material behavior from the Gaussian statistical theory predictions, at small to moderate strains.

It can readily be seen that, when the material behavior exhibits only Gaussian characteristics, Equation (2) reduces to Equation (1) as C_2 supposedly approaches zero.

Equations (1) and (2) apply to the material behavior only in the region of time-independent response; therefore, one must assume that the experimental data are obtained under equilibrium conditions and in the absence of any chemical degradation which occurs in some elastomers and composites at high temperatures. A convenient experimental method used by many investigators to enhance the equilibrium behavior in an elastomeric material is that of swelling the elastomer in a nondegrading solvent. The effect of imbedded liquid (in the swollen material) on Equations (1) and (2) has been accounted for by introducing $V_2^{1/3}$ (volume fraction of gel) and basing the stress on the area of the network structure, A_n. The resulting expression for Equation (2) is

$$\frac{FV_2^{1/3}}{A_n(\lambda - \lambda^{-2})} = 2C_1 + 2C_2/\lambda \qquad (3)$$

where

V_2 = volume fraction of rubber (gel) in the swollen binder

A_n = area of the network structure in the unstrained unswollen state

and the other parameters are as defined previously.

Highly filled systems such as solid propellants present a particularly difficult problem with respect to crosslink density characterization. The bond between filler and binder pulls loose when the material is deformed and therefore equilibrium measurements are almost impossible to obtain.

The technique of solvent swelling [3] provides a useful method of eliminating the binder-filler interaction. It has been shown by Bills and Salcedo [7] that when propellants are immersed in some solvents, the binder swells away from the filler particles, which are then suspended in a "pocket" of solvent within the swollen binder. It may be anticipated, then, that swollen stress-strain measurements of solid propellant samples should allow one to evaluate the binder characteristics alone, free from the confusing interaction effects.

In many cases, the fraction of polymer not connected in the network structure of the binder component (sol fraction) and ineffective in supporting a load may be a significant quantity. Therefore, a correction is required for both the filler fraction and the sol fraction of the binder in the evaluation of the volume swelling ratio and the cross-sectional area of the network structure. The effect of the sol fraction on the swelling ratio of the gumstock (V_2^{-1}) was accounted for by Bills and Salcedo [7] with the following relationship:

$$V_2 = \frac{V_p + V_{st} - V_e}{V_p + V_e/V_b} \tag{4}$$

where

V_p = volume of the specimen in the unstrained unswollen state

V_{st} = volume of solvent in the swollen specimen

V_c = volume of extractable polymer (volume of sol) in the specimen

V_b = volume of binder in the specimen.

The volume fraction of rubber in the network structure (gel) is defined by the following relationship:

$$V_0 = 1 - \frac{V_e}{V_b V_p} , \tag{5}$$

where V_0 is the volume fraction of network structure in the binder component and the other symbols have the same meaning as previously defined. The geometrical equilibrium swelling ratio, Q, is defined by the relationship

$$Q = \frac{V_p + V_{st} - V_e}{V_p} , \tag{6}$$

and substitution of Equations (5) and (6) into Equation (4) with rearrangement yields the following relationship for the determination of V_2:

$$V_2 = \frac{V_0}{Q} . \tag{7}$$

The geometrical equilibrium swelling ratio may be obtained from the specimen dimensions with the assumption of isotropic material behavior in accordance with equation (8):

$$Q = \frac{h^3}{h_i} \tag{8}$$

where h_i is the height of the unswollen unstrained specimen and h is the swollen unstrained height. Bills and Salcedo have demonstrated that Equation (8) is a valid estimation for composite material when the filler-polymer bond releases because the filler particles do not then interfere with the binder swelling behavior. It would then appear that swollen tensile or compression measurements would allow one to evaluate the binder characteristics without the complicated binder-filler interactions.

Section III. LITERATURE SURVEY

In this section the experimental procedure used by several investigators to obtain equilibrium stress-strain data which were subsequently used to determine the crosslink density of elastomeric materials is discussed. It is not intended to be a complete bibliography on the subject but should furnish a starting point for those investigators desiring an extensive literature survey.

Cluff, Gladding, and Pariser [8] determined the crosslink density of a polyurethane gumstock from tensile and compression data:

> Equilibrium compression modulus was measured on the apparatus ... which consisted essentially of a micrometer gauge with plates attached to both ends of the plunger. This assembly was mounted on a stand by a movable clamp so the height could be adjusted to accommodate samples of varying size. The bottom plate was parallel to the bottom of the stand. The elastomer used was a polyether urethane containing carbon-carbon unsaturation and cured with an accelerated sulfur recipe. Three vulcanizates were prepared, each at a different state of cure.
>
> Cylindrical pellets (0.5 in. high and 0.75 in. in diameter) were allowed to swell to equilibrium in toluene after the dimensions had been measured accurately. This required about one week. A swollen pellet was then placed between the bottom plates, and the entire assembly was immersed in enough toluene to cover the pellet completely. This prevented solvent from evaporating from the pellets during the determinations. Weights were placed on the top plate in increasing amounts, and the deflection from the zero reading was recorded for each weight.
>
> Equilibrium extension modulus was measured on an Instron tensile testing machine, Model TT-B (Instron Engineering Corp.). Measured strips, approximately 4 × 0.25 × 0.075 in., were allowed to swell in toluene for six days at 25°C. The degree of swell was determined gravimetrically, and the strips were then elongated to 50% at a crosshead speed of 0.02 in./minute.

The compression and extension methods gave values of effective crosslink density that agreed within 3 percent. Both methods agreed reasonably well with theoretical values calculated from the amount of sulfur used in the vulcanization.

Seely and Dyckes [9] determined the crosslink density of cellular and solid silicon formulations with varying concentrations of crosslinking agents and cell forming compounds:

> Cylindrical specimens approximately 0.46 cm. high and 6.5 $cm.^2$ in cross section were die-cut from cured rubber slabs. These specimens were oven-dried for 2 hr. at 100°C. and then weighed on an analytical balance. Specimen height was measured on a Dice electronic micrometer; six readings were averaged to the nearest ten-thousandth of an inch. ...
>
> The weighed, measured samples were placed in specimen jars and then immersed in selected solvents ... . The samples were allowed to swell until equilibrium swelling was attained (at least 10 days). The temperature was maintained at 23°C. within ±0.5°C. throughout the investigation, including the period of compression-deflection work.
>
> In testing the specimens, a special steel platen tray was mounted on the compression cell of an Instron Tester. The tray was filled with the appropriate solvent and the instrument was calibrated. The swollen specimen was then placed in the tray and subjected to a compression loading at a rate of 0.05 in./min. The test was discontinued when the sample had been deflected approximately 10%. This test was repeated twice after a 1.5-min. recovery period for each test.
>
> ... the method employed here for crosslinking determinations is suitable for cellular rubber, since the data obtained from toluene-swollen specimens agrees quite well with theoretical calculations.

Seeley [10] determined the effective crosslink density for four silicon-filled silicone rubber vulcanizates at different degrees of crosslinking:

> Right-cylindrical test specimens were die-cut from vulcanized rubber sheets. This shape was considered to be less prone to dimensional measurement errors, and the round cross-section would tend to minimize any anomalous swelling effects that might occur at or near the surfaces. The four rubber formulations used in this investigation ... were compounded, and vulcanized with conventional rubber-processing techniques and equipment. Three homologous series of solvents (A. R. grade in most cases) were selected to give a wide range of swelling characteristics: benzene, xylene and toluene; acetone, methyl ethyl ketone (MEK), and methyl propyl ketone (MPK); methanol (MeOH), n-propanol

(n-PrOH), and n-hexanol (n-HexOH). Equilibrium swelling was established (approximately 14 days) at temperatures of 8, 23, 41, and 60°C. ... The compression-deflection measurements were made at a rate of 0.05 in./min. on a Model TTB Instron tester with an environmental chamber attachment. A temperature control of ±0.5°C. was maintained during the swelling times to equilibrium, and the temperature varied no more than 3°C. during the short testing interval at the higher temperatures; the variation was less at the lower temperatures.

Although the compression-deflection data from solvent-swollen silicon rubber vulcanizates relate compatibly with a Gaussian statistical theory, a non-Gaussian statistical approach as proposed by Mooney for high strains accommodates the data more explicity. The explicit equations of state derived for each solvent system are of the Mooney type, involving two independent parameters. Assuming the empirical equations are related to the theoretical Mooney equations, values for the C_1 and C_2 Mooney parameters were determined. The C_1 parameter was found to vary with rubber formulation, solvent action, and equilibrium temperature. However, at 60°C. the temperature dependence became negligible. The C_2 parameter varied with solvent and equilibrium temperature.

Beyer and Carlton [2] used the tensile properties of solvent-swollen propellant and gumstock samples to determine the average molecular weight between crosslinks and hence the crosslink density:

The swollen tensile properties of the propellant samples were measured with cast oval rings (3/16-in.-sq cross section with a 2-in.-long straight section before swelling). ... The swollen properties of the gumstock were measured with milled rings (1-in. diameter with a cross section of 1/10 in. × 1/8 in. before swelling), ...

This test was performed with cast oval rings ... swollen in benzene for at least 5 days. The rings were stretched at a constant rate of 0.1 in./min in the multistation tester. The data were reduced on a computer to give values for the average molecular weight between crosslinks M_c by the relation

$$M_c = \rho v_2^{1/3} RT/G_e$$

where v_2 is the volume fraction of the gel in either the swollen polymer or the propellant corrected for the sol fraction and G_e is the equilibrium shear modulus determined from a Mooney-Rivlin plot.

Kelly [11] used tensile and compression measurements on the solvent-swollen material to determine the crosslink density of polyurethane, polybutadiene, and PBAN propellants:

> Wooden tab end-bonded samples were used exclusively for these measurements. It was found, upon swelling in various solvents, that in many cases the propellant-tab bond was not destroyed, but, in fact, remained stronger than the swollen propellant. Tensile measurements could then be carried out in the swollen state by attaching hooks to the wooden tab ends of the samples and applying the loading device directly through the tabs.
>
> The sample is suspended in a solvent-containing cylinder in a thermostated bath. A chain is attached to the hook at the top end of the sample and also to the scale-pan assembly on a triple beam laboratory balance ... . The other end of the sample is hooked to a rod which extends to the bottom of the cylinder. The rod is rigidly held in place by a ring stand which rests on a laboratory jack.
>
> The load is applied to the swollen sample by moving the riders on the balance, and the laboratory jack is adjusted to zero the reading on the scale. Elongation is measured by a cathetometer which follows the displacement of small bench marks obtained by imbedding short pieces of fine wire in the sample of swollen propellant. The samples reached equilibrium elongations within a few minutes of load application and readings were taken at 10-gram increments. Crosslink density is then determined by utilizing the two constant empirical Monney-Rivlin relationships.
>
> The experimental determination of v_2 was accomplished by linear measurements of samples submerged in solvent for at least four days with a subsequent change in fresh solvent at successive 2-day intervals until equilibrium measurements were obtained. Extraction of thin slices of propellant in a soxhlet apparatus was attempted with various solvents until a system was achieved which did not degrade the network. This determination was made by plotting weight extracted against extraction time, and the attainment of a reasonably level plateau was taken to indicate complete extraction

without degradation. Ethylene chloride was adopted as the most useful solvent for the swelling and extraction procedures. Since the ammonium perchlorate filler was somewhat soluble in ethylene chloride, a water wash was applied to the extract before filtration and separation of the organic phase. The extracted polymer solution was then concentrated and dried to constant weight in a small rotary evaporator.

Several preliminary attempts to determine cross-link density by swollen compression techniques as described by Cluff, Gladding and Pariser [8] on unfilled rubbers and by Seeley and Dyckes [9] on cellular foams showed fairly good agreement with tensile tests in some cases, but the scatter was generally greater for the filled systems.

Landel and Tschoegl [12] utilized the tensile and compression data on swollen SBR samples to determine the equilibrium modulus of SBR rubber:

> Rings were cut from SBR sheets ... and were swollen in toluene. The diameters of each individual ring were measured with a traveling microscope. The swollen rings had outer diameters of about 2.5 inches and inner diameters of about 2.2 inches. The thickness and the width of the swollen rings were both about 0.3 inches providing a virtually square cross section. The tests were made in the Instron tester at room temperature with the rings fully immersed in the solvent at all times. At least two, but in some cases more, rings were pulled at crosshead speeds of 0.02, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 inches per minute.
>
> Data were obtained in uniaxial compression on swollen SBR cylinders of about 1.5 inch diameter and 1.5 inch height in the swollen state. The test specimens were molded separately and had parallel end faces. The tests were made at room temperature and at crosshead speeds of 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 inches per minute. The specimens were fully immersed in the toluene during the compression.

The equilibrium modulus was determined from plots of nominal stress versus the corrected neo-hookean strain and from plots of Mooney stress, $\sigma/(\lambda - \lambda^{-2})$ versus $1/\lambda$. Although different values of equilibrium modulus were obtained from compression and tension data, from the results presented it can be concluded that the behavior of the swollen rubber in both uniaxial tension and compression is neo-hookean up to break. The absence of any systematic effect of the extension rate on the measurements over three decades of crosshead speeds indicated the mechanical and ultimate properties of the swollen rubber

are independent of time within the experimental error. The only effect of temperature was found to be that predicted by the kinetic theory of rubber elasticity.

Martin [13,14] utilized the tensile and compression measurement on both filled and unfilled PBAA and CTPB fomulations to determine the crosslink density:

> Specimens of each formulation ... were allowed to swell in benzene for several days. The specimen dimensions were measured periodically to determine when equilibrium swelling was obtained. The geometrical swelling ratio was determined, and the assumption of isotropic swelling condition was verified. The compression deflection and tensile deflection measurements were made on an Instron Model TTB Tester at displacement rates of 0.02 inch per minute. The compression specimens were approximately 1/2-inch cubes in the unstrained unswollen state.
>
> ... The binder stress-strain characteristics were determined using a cast ring approximately 1 inch in outside diameter, 3/8-inch wide, and 1/8-inch thick. The stress-strain characteristics of the composite material were determined using die cut ring specimens approximately 1 inch in outside diameter, 1/4-inch wide, and 1/4-inch thick ... in the unstrained, unswollen state. The specimens were submerged in the solvent during the test.

Plots of Mooney stress versus the reciprocal of the extension ratio were then used to determine the crosslink density.

The methods of determining the equilibrium stress-strain behavior of gumstock and propellants at equilibrium swelling conditions discussed in this section are basically divided into two types. The method of placing or hanging a dead weight on the sample and waiting for equilibrium deformation to occur is both cumbersome and tedious. The method of measuring the compression and tension properties of the swollen material at a constant low rate of deformation seems to be more desirable since it eliminates the possibility of damaging the swollen network structure by removing or placing weights on the sample by hand.

Section IV. EXPERIMENTAL PROCEDURES

In this section is discussed the recommended experimental procedure including the sample preparation, swelling measurements, and the physical properties measurements at equilibrium swelling conditions. Perhaps the most difficult experimental problem involves the handling and clamping of the fragile swollen network in preparation for tensile and compressive stress-strain measurements. The sample configuration and technique described here eliminate most of this difficulty.

1. Sample Preparation

The tensile stress-strain properties at equilibrium swelling conditions for gumstocks and composite propellants are determined by using either cast, milled, or stamped ring samples. The gumstock sample should be approximately 3/4 inch outside diameter, 1/2 inch inside diameter, and 1/4 inch wide in the unstrained, unswollen condition. The composite samples should be approximately 1.0 inch outside diameter, 1/2 inch inside diameter, and 1/4 inch wide in the unstrained, unswollen condition. The compression force-deflection measurements on gumstocks and composite propellants at equilibrium swelling conditions are made on either cast, milled, or stamped right circular cylinders. Both the gumstock and propellant sample dimensions should be right circular cylinders approximately 1/2 inch in diameter and 1/2 inch high in the unstrained, unswollen state. The area and height of the specimens do not restrict the use of the Mooney relation for calculating the crosslink density at least for reasonable dimensions. However, the specimen height-to-diameter should be smaller than a one-to-one ratio to prevent skewing under compression which would yield unrealistic compression-deflection data.

2. Solvent Selection

While no one solvent is used by all investigators in the swelling of polymeric material, benzene and toluene appear to be the solvents most commonly used. However, one should choose a solvent that will not degrade the cured network. Preliminary extraction experiments on thin slices of the gumstock in a soxhlet apparatus using various solvents will allow one to determine a system that will not degrade the network of the cured material. The cured material is periodically removed from the soxhlet apparatus, dried in an oven, and weighed. A plot is then made of extracted weight versus the extraction time. The attainment of a reasonable level plateau in extracted amount should then indicate that complete extraction may be obtained with the solvent without degradation to the network structure.

3. Swelling Ratio

After a suitable solvent has been chosen the gumstock and composite material is allowed to reach equilibrium swelling conditions in the solvent. Prior to placing the specimens in the solvent, they are weighed and measured. The weight in grams should be recorded to the fourth decimal place. The specimen measurements should be recorded to at least the nearest one-thousandth of an inch. The measurements should be taken with use of dial gage, cathatometer, or similar instruments. The specimens are to be swelled preferably in a dark place at a controlled temperature of approximately 75°F. The specimen dimensions are to be determined each day and recorded. The solvent should be replaced with fresh solvent at two-day intervals until equilibrium swelling is obtained. Equilibrium swelling is assumed to be obtained when the specimen dimensions are the same for three consecutive days.

The geometrical swelling ratio of the specimen is then determined as follows:

$$Q = \frac{h^3}{h_i^3} \quad , \tag{9}$$

where

Q = geometrical swelling ratio

h_i = unswollen, unstrained height

h = swollen, unstrained height.

The volume fraction of extractable polymer in the binder is approximated as

$$V_e = \frac{w_i - w_f}{w_b} \quad , \tag{10}$$

where

V_e = volume fraction of extracted polymer

w_i = initial dried weight of sample

w_f = final dried weight of sample

w_b = initial weight of binder in the sample.

The volume fraction of binder in the swollen network structure (gel phase), V_0, is given by the relationship:

$$V_0 = 1 - V_e \quad . \tag{11}$$

Therefore, the equilibrium swelling ratio for the binder is

$$V_2^{-1} = \frac{Q}{V_0} \quad , \tag{12}$$

where V_2^{-1} is the equilibrium swelling ratio of the binder.

The cross-sectional area of the network structure is then

$$A_n = A_i V_0^{2/3} \quad , \tag{13}$$

where

A_n = cross-sectional area of network structure in the specimen in the unswollen, unstrained state

A_i = cross-sectional area of the specimen in the unstrained, unswollen state.

4. Force-Deflection Measurements

Various investigators have used different apparatus for determining the force-deflection measurements on swollen polymeric material. The recommended method for determining the force-deflection measurements is the use of the apparatus given in Figures 1 and 2 in conjunction with an Instron or similar type testing machine. The apparatus used for the swollen tensile tests is presented in Figure 1 and consists of a glass cylinder fitted with closures at both ends with a suitable seal at the bottom for the pull rod. The bottom rod is fastened to the crosshead; the top rod is fastened to a load cell. The swollen ring is placed over the fixtures as shown and the cylinder is filled with the solvent. The compression tests are conducted with the setup shown in Figure 2. A flat plate is attached to a load cell mounted on the bottom of the crosshead of the Instron machine (Figure 2). The swollen specimen is placed in the position shown and the pan is filled with the solvent. As the crosshead moves down compressing the sample, the force on the sample is recorded on the Instron chart.

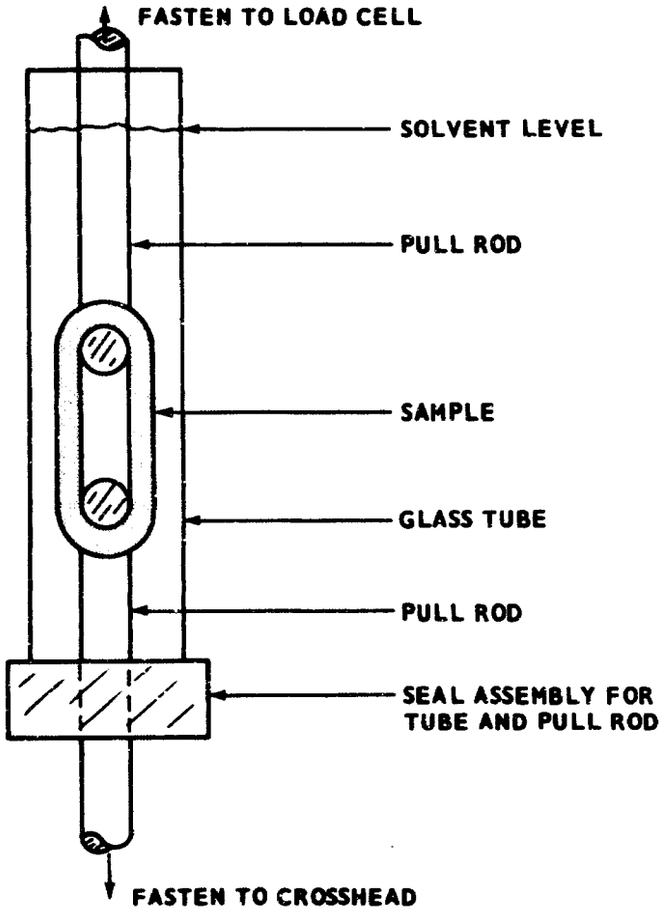


FIGURE 1. EQUIPMENT FOR TENSILE STRESS-STRAIN MEASUREMENTS ON SOLVENT SWOLLEN MATERIALS

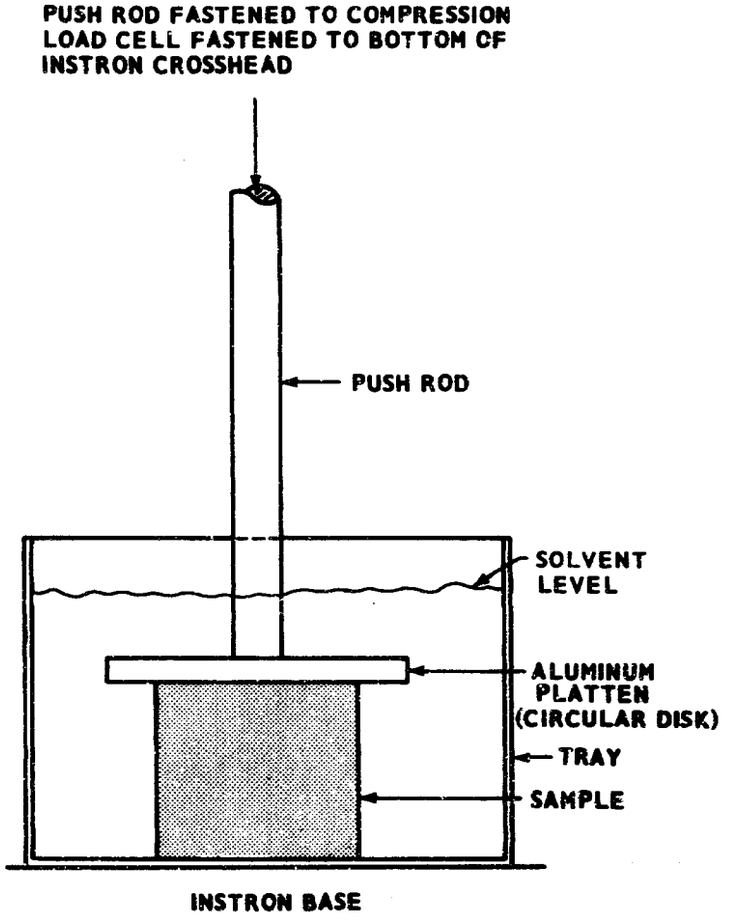


FIGURE 2. EQUIPMENT FOR COMPRESSIVE STRESS-STRAIN MEASUREMENTS ON SOLVENT SWOLLEN MATERIALS

Both the tensile and compression measurements are obtained at crosshead displacement rates of 0.02 inch per minute. When the crosshead displacement rate and the chart speed are known, the force-deflection measurements are obtained from the Instron load-time chart. It is important that the specimen be submerged in the solvent during the tests to prevent surface cracks from forming on the specimen during the test due to solvent evaporation.

Section V. CROSSLINK DENSITY CALCULATIONS

The Mooney-Rivlin expression for describing the equilbrium stress-strain behavior of polymers was given by Equation (3) as

$$\frac{FV_2^{1/3}}{A_n(\lambda - \lambda^{-2})} = 2C_1 + 2C_2/\lambda \quad . \tag{3}$$

Equation (3) indicates that a plot of $\frac{FV_2^{1/3}}{A_n(\lambda - \lambda^{-2})}$ versus $1/\lambda$ will yield a straight line of zero slope provided $C_2 \rightarrow 0$. However, C_2 is not always zero for all swollen polymeric materials but in most cases Equation (3) can still closely approximate the material's stress-strain behavior. The crosslink density is then determined from the intercept of $1/\lambda = 0$ and the straight line drawn through the experimentally determined points.

The equilibrium stress-strain behavior of a CTPB formulation will be used to illustrate the crosslink density calculations. Some representative Mooney-Rivlin plots for several CTPB gumstock and composite formulations swollen in benzene are presented in Figures 3 and 4. The compression-deflection data $\left(\frac{1}{\lambda} > 1\right)$ yield a straight line of zero slope as expected. However, for the tensile-elongation data $\left(\frac{1}{\lambda} < 1\right)$, the initial value of $\frac{FV_2^{1/3}}{A_n(\lambda - \lambda^{-2})}$ was lower than the compression-deflection data near $\frac{1}{\lambda} = 1$ but tended to approach the values obtained from the compression data at higher elongations. The tensile data, treated in this way, yielded a straight line with a negative slope. Since straight lines through both the tensile and compression data have the same intercept at $\frac{1}{\lambda} = 0$, both tensile and compression data indicate the same crosslink density values.

For formulation no. 7 of Figure 3, both the compression and tensile data indicate an intercept of $\frac{1}{\lambda} = 0$ at $\frac{FV_2^{1/3}}{A_n(\lambda - \lambda^{-2})} = 1000\ gm/cm^2$. From Equation (2), $2C_1 = 1000\ gm/cm^2$. The term C_1 is defined as the Gaussian term in Flory's equation, and

$$\nu_e = \frac{2C_1}{RT} , \tag{14}$$

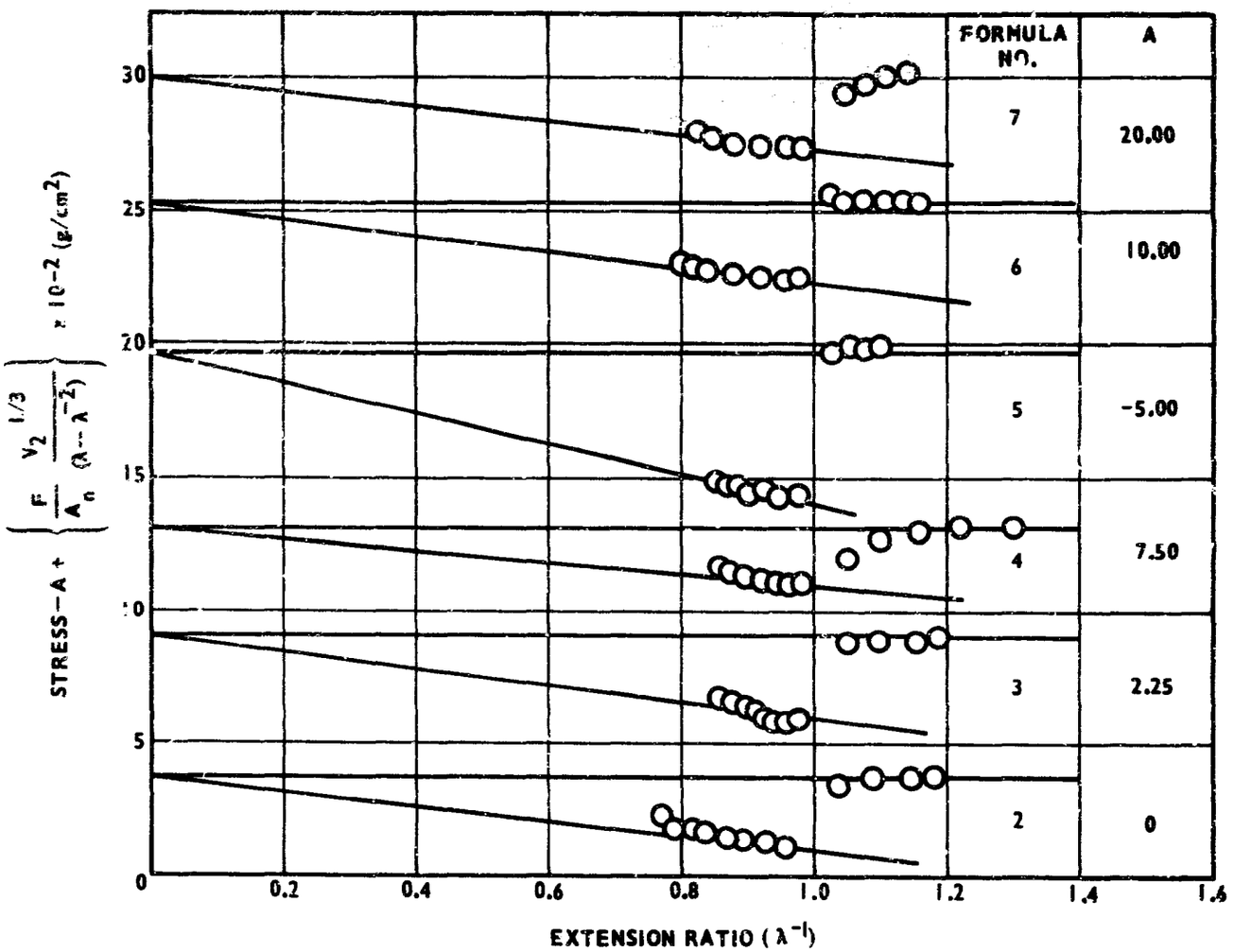


FIGURE 3. MOONEY-RIVLIN PLOT FOR CTPB GUMSTOCK, SWOLLEN IN BENZENE

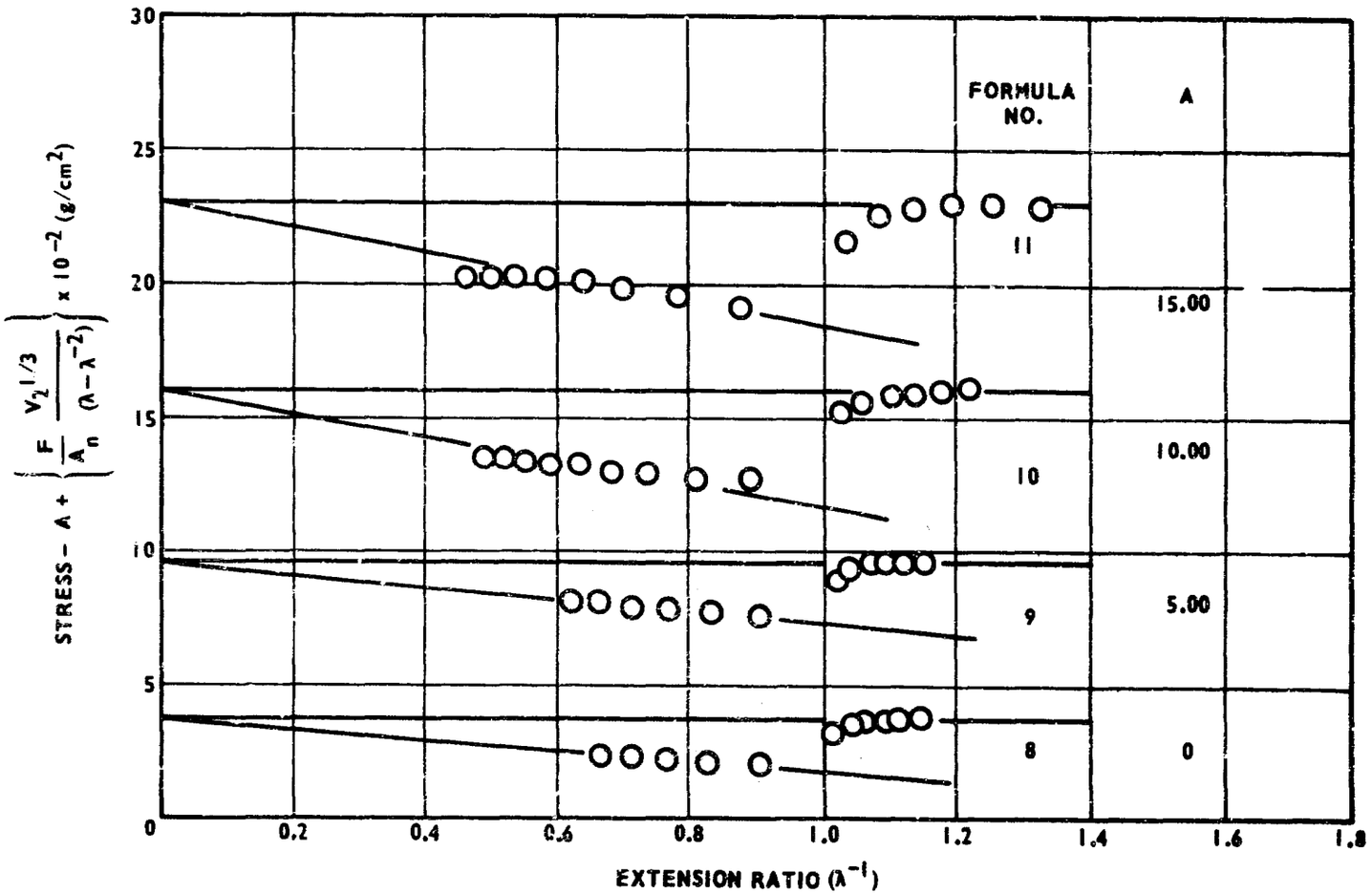


FIGURE 4. MOONEY-RIVLIN PLOT FOR CTPB COMPOSITES WITH VARIOUS FILLER CONTENT SWOLLEN IN BENZENE

where

ν_e = effective crosslink density (moles/cm^3)

$2C_1$ = 1000 g/cm^2

R = 8.479 × 10^4(g-cm/mole, °K)

T = 77°F = 295°K.

With these values substituted into Equation (14),

$$\nu_e = \frac{1000\ \text{g/cm}^2}{(8.479 \times 10^4\ \text{g-cm/mole-°K})\ (295\text{°K})} = 4.0 \times 10^{-5}\ \text{moles/cm}^3 \ .$$

The plots in Figures 3 and 4 are offset by the amount A for convenience in presenting the data. Crosslink density determinations should be conducted on at least four different samples of each formulation tested and the average reported.

Section VI. CONCLUSIONS

The method of determining crosslink density considered in this discussion minimizes the difficulty inherent in the determination of the effective crosslink density without sacrificing the reliability of the results obtained.

It is of interest to also examine the statistical variation of the crosslink density data determined from stress-strain measurements on solvent swollen samples. Very little information could be found in the literature that indicates the variations of crosslink density values observed by the investigators using this method. Table I presents the variations observed by Martin,* Landel [12], and Seeley [10]. Martin's data (material No. 2-11) were obtained on PBAA gumstock and composite formulations. The data reported were obtained on four different samples, two swollen in benzene and two swollen in methylene chloride. The coefficient of variation observed on gumstock formulations (No. 2-7) ranged from 2.3 to 9.8 percent. The coefficient of variation observed for PBAA composite formulations (No. 8-11) ranged from 3.8 to 10.5 percent. Landel's data were obtained on SBR samples swollen in toluene. Crosslink density values were determined from the equilibrium modulus data reported. Different mean values were obtained by Landel from tension and compression measurements. A coefficient of variation of 8.1 percent was observed in the data from tensile measurements and a coefficient of variation of 5.8 percent was determined for the data from compression measurements.

Seeley's data (No. 13 and 15) were obtained on two formulations of silicone rubber. At least four determinations were made on samples swollen in benzene, toluene, and methylethylketone. The coefficient of variation determined from Seely's data ranged from 3.0 to 11.2 percent.

The data presented in Table I indicate that variations in crosslink density values determined from stress-strain measurements on solvent swollen samples should be within ±10 percent of the mean value. This fact indicates the importance of obtaining crosslink density values on at least four different samples of each formulation investigated. Increasing the number of samples will be desirable and should increase the confidence in the mean crosslink density value obtained.

---

*Martin, D. L., Jr., Laboratory Investigation — Unpublished Results, Army Propulsion Laboratory and Center, U. S. Army Missile Command, Redstone Arsenal, Alabama, 1968.

TABLE I. CROSSLINK DENSITY DATA

Material	ν_e Mean (moles/cm^3 × 10^5)	Standard Deviation	Coefficient of Variation (%)	Solvent
PBAA-2	4.26	0.237	5.6	Benzene and $CHCl_3$
PBAA-3	2.05	0.047	2.3	Benzene and $CHCl_3$
PBAA-4	3.02	0.158	5.2	Benzene and $CHCl_3$
PBAA-5	6.71	0.655	9.8	Benzene and $CHCl_3$
PBAA-6	2.37	0.134	5.7	Benzene and $CHCl_3$
PBAA-7	1.20	0.074	6.2	Benzene and $CHCl_3$
PBAA-8	9.93	1.041	10.5	Benzene and $CHCl_3$
PBAA-9	6.25	0.235	3.8	Benzene and $CHCl_3$
PBAA-10	3.86	0.277	7.2	Benzene and $CHCl_3$
PBAA-11	1.14	0.117	10.3	Benzene and $CHCl_3$
SBR-12-T	2.84	0.229	8.1	Toluene
SBR-12-C	3.53	0.206	5.8	Toluene
Silicone 13	3.42	0.281	8.2	Benzene
Silicone 13	3.26	0.365	11.2	Toluene
Silicone 13	3.20	0.214	6.7	MEK
Silicone 15	4.41	0.314	7.1	Benzene
Silicone 15	4.54	0.136	3.0	Toluene
Silicone 15	4.09	0.352	8.6	MEK

REFERENCES

1. Martin, D. L., Jr., "Microstructural Response and Failure in Solid Propellants," ICRPG Mechanical Behavior Working Group, 1, 5th Meeting, 1966, p. 191.

2. Beyer, R. B., and Carlton, C. H., Research to Relate the Fffects of Structure and Composition of a Propellant Binder to the Mechanical Properties of a Composite Propellant, Research and Advance Technology Department, United Technology Center, Sunnyvale, California, November 1966, Report No. UTC 2147-FR.

3. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

4. Flory, P. J., and Rehner, J., Jr., "Statistical Mechanics of Crosslinked Polymer Networks," J. Chem. Phys., 11, 1943, p. 512.

5. Mooney, M., "A Theory of Large Elastic Deformation," Journal of Applied Physics, 11, 1940, p. 582.

6. Rivlin, R. S., and Thomas, A. G., "Rupture of Rubber, Part 1, Characteristics Energy for Tearing," Journal of Polymer Science, 10, No. 3, 1953, p. 291.

7. Bills, K. W., and Salcedo, F. S., "The Swelling of Unfilled and Highly Filled Polymers," J. Appl. Phys., 32, November 1961, p. 2364.

8. Cluff, E. F., Gladding, E. K., and Pariser, R., "A New Method for Measuring the Degree of Crosslinking in Elastomers," Journal of Polymer Science, 45, 1960, p. 341.

9. Seeley, R. D., and Dyckes, G. W., "Determination of Effective Crosslink Density in Silicone Rubber," J. Appl. Polymer Science, 9, 1965, p. 151.

10. Seeley, R. D., "Characterization of Silicone Rubber Vulcanizates. Part I: Solvent, Temperature, and Specimen Shape Effect on Effective Crosslink Density Determinations," J. Appl. Polymer Science, 9, 1965, p. 3049.

REFERENCES (Concluded)

11. Kelly, F. N., Microstructural Response and Tensile Failure Mechanisms in Solid Propellants, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California, April 1965, Report No. AFRPL-TR-65-86.

12. Landel, R. F., and Tschoegl, N. W., A Research Program on Solid Propellant Physical Behavior, California Institute of Technology, Materials Science-Polymer Laboratory, June 1967, Report No. AFRPL-TR-67-193.

13. Martin, D. L., Jr., "The Influence of Microstructural Characteristics on the Maximum Strain Energy Density of a Composite Propellant," ICRPG Mechanical Behavior Working Group, 1, 6th Meeting, 1966, p. 277.

14. Martin, D. L., Jr., Microstructural Characteristics and Failure Mechanism for a Carboxyl Terminated Polybutadiene Composite System, U. S. Army Missile Command, Redstone Arsenal, Alabama, September 1968, Report No. RK-TR-68-16.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Army Propulsion Laboratory and Center Research and Engineering Directorate U. S. Army Missile Command Redstone Arsenal, Alabama 35809	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP NA

3. REPORT TITLE

CROSSLINK DENSITY DETERMINATIONS FOR POLYMERIC MATERIALS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report

5. AUTHOR(S) (First name, middle initial, last name)

Donald L. Martin, Jr.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
28 January 1970	31	14

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. (DA) 1M262302A211 AMC Management Structure Code No. c. 522C.11.585 d.	RK-TR-70-6 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AD _____

10. DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of this Command, ATTN: AMSMI-RK.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	Same as No. 1

13. ABSTRACT

Chemical crosslinking of polymeric binders is possibly the most significant factor affecting the mechanical behavior of unfilled and highly filled elastomers. There are basically two physical methods used by various investigators for experimentally determining the degree of crosslinking in elastomeric materials. These are the swelling method using Flory's equation and the equilibrium stress-strain method. The procedure discussed in this report is recommended as a tentative standard procedure to be followed in the collection of equilibrium stress-strain data and in the use of these data in the determination of the effective crosslink density of polymeric binders and composite propellants.

DD FORM 1 NOV 68 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chemical crosslinking **Polymeric binders** **Swelling method** **Equilibrium stress-strain method** **Composite propellants**						